



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 253 159 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
30.10.2002 Bulletin 2002/44

(51) Int Cl.7: C08G 18/10, C09J 175/08

(21) Application number: 02008125.3

(22) Date of filing: 11.04.2002

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 12.04.2001 US 833453

(71) Applicant: **AIR PRODUCTS AND CHEMICALS,
INC.
Allentown, PA 18195-1501 (US)**(72) Inventors:

- Paulsen, Evelyn Jennifer Lin
Macungie, PA 18062 (US)

- Smith, Andrea Karen
Macungie, PA 18049 (US)

(74) Representative: **Schwabe - Sandmair - Marx
Stuntzstrasse 16
81677 München (DE)**

Remarks:

A request for correction of the claims has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) Controlled structure polyurethane prepolymers for polyurethane structural adhesives

(57) A structural polyurethane adhesive composition comprising a polyurethane reaction product and a curative for isocyanate groups, characterized in that the polyurethane reaction product consists essentially of at least 80 wt% perfect prepolymers and less than 2 wt% free isocyanate monomer.

Description**FIELD OF THE INVENTION**

5 [0001] This invention relates to polyurethane structural adhesives comprising a controlled structure isocyanate terminated prepolymer.

BACKGROUND OF THE INVENTION

10 [0002] More sophisticated production and new applications demand that adhesives deliver increased performance and stronger, more resistant bonds. For example, the adhesive may be required to adhere to poorly prepared, contaminated substrates without a primer. They may also be expected to display non-sag properties upon application to vertical surfaces, have rapid green strength development, and form bonds that can withstand elevated temperature exposure.

15 [0003] Polyurethane structural adhesives have been used for many years in industry to adhere substrates like fiberglass reinforced polyesters (FRP). US 3,936,051 discloses typical commercially available polyurethane structural adhesives. The typical adhesive comprises an isocyanate functional component, e.g. a polyurethane prepolymer, and a curing agent. The prepolymer component is the reaction product of polypropylene glycol and toluene diisocyanate, and the curative is a blend of polypropylene ether glycol and N,N,N',N'-tetrakis (2-hydroxypropyl) ethylene diamine.

20 These adhesives are well known for their good flexibility and ability to adhere difficult substrates like FRP. They are also known for superior bonding of dissimilar substrates like FRP to cold rolled steel (CRS).

[0004] A common approach to improving adhesive properties is to focus on the curative component of the two component (2K) urethane adhesive system. The objective of many of these innovations is to impart non-sag properties to the applied adhesive. Non-sag adhesives can be applied to substrates in a vertical position without the adhesive dripping or sagging before the second substrate is placed over the adhesive.

25 [0005] US 3,714,127 discloses the addition of di- and multi-primary amines to a 2K polyurethane-based adhesive to impart sag resistance.

[0006] US 4,336,298 discloses the addition of *para*- or *ortho*-phenylene diamine to a curative blend to improve sag resistance of an adhesive system for bonding fiberglass reinforced polyester (FRP) panels.

30 [0007] US 5,508,111 discloses the use of aryl or aromatic amines, like 1,8-naphthalene diamine, in polyurethane adhesives for good sag properties.

[0008] US 4,444,976 discloses secondary diamines can also be added to a curative for a 2K polyurethane adhesive to give non-sag properties.

[0009] US 5,002,806 discloses a mixed curative containing a slow and fast reacting diamine for sag resistance in 2K structural primerless urethane adhesives.

35 [0010] Another approach is to add special additives to enhance the adhesive performance. US 5,955,199 discloses the use of polyalldimine or polyketimine in the curative component of a 2K urethane structural adhesive.

[0011] US 4,726,710 discloses the use of bicyclic amide acetals in an antifoaming 2K polyurethane adhesive.

40 [0012] US 5,175,228 discloses a 2K polyurethane composition in which the prepolymer component contains a primary hydroxyl intermediate and has a sufficiently large excess of free isocyanate so that the ratio of free NCO groups in the prepolymer component to OH curative groups plus any amine groups in the curative component is from about 1.2 to about 2.0.

[0013] EP 0 279 566 discloses better adhesion to sheet molding compound (SMC) by incorporating a graft copolymer of poly(alkylene oxide) polyol and a vinyl monomer into a 2K polyurethane adhesive formulation.

45 [0014] US 4,923,756 and 5,143,996 disclose the addition of small amounts of aliphatic polyisocyanates, like m-xylylene diisocyanate, promote primerless adhesion.

[0015] The current polyurethane structural adhesive patent art does not fully exploit the benefits of controlling the structure of polyurethane prepolymers. Current prepolymers specified in these patents are typically produced from the reaction of a polyisocyanate with a polyol in a 2:1 equivalents ratio. The manufacturer may change the type of polyisocyanate or polyol, but the ratio, and therefore the prepolymer distribution (2:1 adducts, 3:2 adducts, etc.) remains unoptimized. Instead, optimization often focuses, as illustrated by the previous patents, on the composition of the curative and different additives that are added to the formulation.

50 [0016] EP 0 827 995 discloses hot melt adhesives comprising a polyisocyanate prepolymer prepared by reacting a polyisocyanate with a functionality of at least 2 with a polyol with a functionality of at least 2, the reaction product comprising at least 90 wt% "perfect" prepolymer and less than 2 wt% unreacted isocyanate monomer and the prepolymer having a free NCO functionality ranging from 0.2 to 8 wt%.

55 [0017] A great deal of work has gone into improving two component polyurethane structural adhesive formulations through improvements in curative, primers, surface treatment and addition of various additives. However, tailoring of

the chemical composition of the isocyanate functional component, or prepolymer, has yet to be fully explored as a means to improve the properties and performance of polyurethane structural adhesives. We have found unexpected advantages in using controlled isocyanate terminated prepolymers that contain controlled levels of residual isocyanate monomer and oligomer content.

5 SUMMARY OF THE INVENTION

[0018] The present invention is directed to a non-solid polyurethane structural adhesive composition comprising a controlled structure isocyanate terminated prepolymer composition having controlled, low levels of residual isocyanate monomer and oligomer content and a curative for isocyanate groups. The residual, or free, isocyanate monomer content is less than 2 wt% of the prepolymer composition.

[0019] The prepolymer composition composing the urethane structural adhesive composition is the product resulting from the reaction of a polyester or polyether polyol containing "n" (at least 2) OH groups and a polyisocyanate. The polyisocyanate prepolymer reaction product comprises oligomers and "perfect" prepolymers. The requisite low oligomer content of the prepolymer composition is ≤ 20 wt% or, reciprocally, can be expressed in terms of its "perfect" prepolymer content which should be ≥ 80 wt%. A "perfect" prepolymer in terms of stoichiometry is a prepolymer of n polyisocyanate molecules and one polyol molecule. The stoichiometric proportions for the polyisocyanate and polyol in the reaction products are 2:1 in the case of diols and 3:1 for triols. The perfect prepolymer is essentially an adduct containing only one molecule of the polyol in each prepolymer molecule. The invention requires that this polyisocyanate prepolymer reaction product (1) consists essentially of at least 80 wt% of a stoichiometric "perfect" prepolymer and (2) contains less than 2 wt% unreacted polyisocyanate monomer.

[0020] By "structural adhesive" we mean a load bearing adhesive, i.e., an adhesive that hardens to afford a relatively high modulus and high strength and may be used to join relatively rigid substrates so that a truly load bearing joint is constructed. Structural adhesives differ from laminating adhesives which are non-load bearing and from hot melt adhesives which are solid materials that are melted at elevated temperatures and applied in liquid form to the substrate.

[0021] Also provided is a method for adhesively joining or sealing two substrates using such structural polyurethane adhesive composition. The method generally comprises

- 30 (1) applying onto a substrate a non-solid urethane structural adhesive composition comprising the controlled structure polyisocyanate prepolymer reaction product having the defined low levels of oligomers and free isocyanate monomer and a crosslinking agent, and
- (2) contacting the adhesive composition disposed on the substrate to a second substrate such that a bond is formed.

"Non-solid" includes pastes and viscous liquids.

35 [0022] Advantages associated with the use of such controlled structure isocyanate prepolymers include

- 40 • an ability to formulate structural adhesives that show improved cured adhesive strength for bonding sheet molding compound compared to those formulated using conventionally prepared isocyanate terminated prepolymers,
- an ability to formulate structural adhesives demonstrating improved ultimate adhesive strength
- an ability to formulate structural adhesives showing improved ambient, or room, temperature development of strength
- the ability to tailor oligomer content and monomer content for controlling properties like viscosity, processability, and the health and safety benefits associated with lower levels of volatile diisocyanate monomer content.

45 DETAILED DESCRIPTION OF THE INVENTION

[0023] This invention relates to the use of certain polyurethane prepolymer compositions in structural adhesives. These prepolymers are controlled structure polyurethane prepolymers comprising the reaction product of a polyisocyanate (A) having a functionality (f) of at least two, with a polyester or polyether polyol (B) of functionality (f) ≥ 2 . The prepolymer reaction product should contain prepolymer-NCO content ranging from 0.2 to 15 wt%. The molecular weight distribution, i.e. distribution of perfect prepolymer to high order oligomers, is controlled in these prepolymer compositions, as well as the amount of free isocyanate monomer content. Thus the prepolymer compositions contain prepolymer-NCO content ranging from 0.2 to 15 wt% and less than 2 wt%, preferably less than 0.5 wt%, unreacted isocyanate monomer. At least 80 wt%, preferably 90 wt%, and most desirably 95 wt%, of the prepolymer reaction product obtained by the reaction of the polyisocyanate with the polyol should comprise a "perfect" prepolymer.

[0024] A "perfect" prepolymer, or adduct, is the perfect endcapping product of polyol B with nA (n polyisocyanate molecules), where n = the functionality (f) of B. For a difunctional B (n = 2), the perfect prepolymer is represented as A:B:A. Oligomers are any species with a composition greater than the perfect 2:1 molecular ratio (A:B:A), for example

3:2 (A:B:A:B:A) or 4:3 (A:B:A:B:A:B:A). For a trifunctional B ($n = 3$), the perfect prepolymer is represented as B:3A. Oligomers in this instance are any species with a composition greater than the perfect 3:1 molecular ratio.

[0025] For example, Airthane® prepolymers marketed by Air Products and Chemicals, Inc. are controlled structure prepolymer compositions. These prepolymer compositions based on TDI and IPDI contain >90 wt% perfect 2:1 prepolymer, i.e., <10 wt% oligomer, and <0.1 wt% residual monomeric isocyanate.

[0026] The urethane structural adhesive composition used in the present method comprises an NCO-terminated urethane prepolymer (also called a polyisocyanate prepolymer) prepared by reacting a polyisocyanate having an NCO functionality of at least 2 with a polyol, preferably performing the reaction in an NCO to active hydrogen equivalent ratio of ≥4:1, preferably, 6-10:1. The unreacted polyisocyanate monomer in the prepolymer reaction product is removed by distillation or other treatment to a concentration of less than 2%, preferably, less than 0.1%. The prepolymer reaction product should contain free isocyanate, i.e., prepolymer-NCO content, ranging from 0.2 to 15 wt%, preferably, 0.5 to 8 wt%.

[0027] Such prepolymers useful in the structural adhesive composition may be prepared according to the teachings of U.S. 4,786,703 and 5,202,001, which disclosures are incorporated by reference.

[0028] The prepolymer reaction products are prepared using suitable organic polyisocyanates well known in the art including, for example, hexamethylene diisocyanate, phenylene diisocyanate, toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI) and bis-(4-isocyanato cyclohexyl) methane. Especially suitable are the 2,4- and 2,6-TDIs individually or together as their commercially available mixtures with the percentages being from about 65-100% of the 2,4- and 0-35% of the 2,6-isomer by weight. Other suitable isocyanate mixtures of diisocyanates known commercially as "crude MDI", also known as PAPI, which contain about 60% MDI along with other isomeric and analogous higher polyisocyanates.

[0029] Polyether and polyester polyols are commonly used in the preparation of polyurethane prepolymers. The hydroxyl-terminated polyethers are typically polyalkylene ether glycols, such as poly(ethylene ether) glycol, poly(propylene ether) glycol and polytetramethylene ether glycol. Other polyethers are prepared by the copolymerization of cyclic ethers, such as ethylene oxide, propylene oxide and trimethylene oxide with various aliphatic diols such as ethylene glycol, butane diols, e.g., 1,3- and 1,4-butane diols, and the like. Polyester polyols can also be used for producing the polyurethane prepolymers, and these would include hydroxyl terminated polyesters such as ethylene adipate, polypropylene adipate, polyhexamethylene adipate and copolymers prepared by copolymerizing ethylene glycol and propylene glycol with the above polyesters, which include poly(1,4-butylene-ethylene) adipate and poly(1,4-butylene-propylene) adipate.

[0030] The above polyether and polyester polyols are conventional for producing polyurethane prepolymers and can be blended such that the polyol composition (single or blend) used in making the prepolymer typically has an average Mn ranging from about 1000 to 60,000, and typically from 4200 to about 25,000.

[0031] In the preferred prepolymer synthesis, it is important to maintain a high equivalent ratio of TDI to the polyol, e.g., a range from 4 to 20:1. As the level of TDI to polyol approaches 4:1 and then stoichiometric, greater quantities of higher molecular weight oligomers are formed which detract from the performance characteristics of the urethane prepolymer adhesive composition. Preferably, the equivalent ratio of TDI to polyol in the reaction is from 6 to 10:1 equivalents of TDI to polyol to produce oligomers at less than 20 wt%, preferably less than 10 wt%.

[0032] Maintaining a high equivalent ratio of feed TDI to polyol is extremely important because when the equivalent ratio of TDI to polyol is lowered to slightly above stoichiometric, e.g., 10% excess, which is conventional, oligomers are formed. Higher oligomer formation results in lower performance properties and higher prepolymer viscosity.

[0033] In addition to the polyisocyanate prepolymer, the urethane structural adhesive composition contains a curative composition as is well known in the art. Suitable curatives comprise diamines, polyols, or blends thereof, as well as optional catalyst, thickening agent, or drying agent. Examples of diamines include both aromatic and aliphatic diamines, primary and secondary amine terminated polyether polyols, and difunctional, trifunctional, and polymeric amines. Examples of polyols include polyester or polyether polyols, which can be diols, triols and tetrols, having primary, secondary and/or tertiary alcohol groups. These polyols may be mixed with the diamines. Optional catalysts include tertiary amine catalysts and suitable organometallic catalysts, such as those derived from tin, zirconium, and bismuth. Other optional additives include thickening, coloring and drying agents.

[0034] Substrates that may be bonded with the adhesive include cold rolled steel, aluminum, fiberglass reinforced polyester (FRP), sheet molding compound (SMC), ABS, PVC, polycarbonate, polypropylene, TPO, wood, and glass.

[0035] The following materials were used in the Examples:

Arcok® PPG 2025, from Bayer Corp.

55 Quadrol® polyol from BASF Corp.

Microtuff 325F talc from Barretts Minerals Inc.

Cab-o-sil TS 720 fumed silica from Cabot Corp.

Aluminum Powder, 325 Mesh, Grade 101 from Toyal America Inc.

Microbeads (10 mil and 20 mil) from Cataphote.
 Zinc coated cold rolled steel (Zn CRS) from ACT Laboratories, Inc.
 Sheet molding compound (SMC) - GC7113- from GenCorp.
 Polyurethane prepolymers shown in Table 1

5

Table 1

Prepolymer	Isocyanate	Polyol	% NCO	Residual Diisocyanate (wt%)	% Oligomer
10	1	MDI	PPG-Based	6.6	0.4
	2	MDI	PPG-Based	6.6	>5
	3	MDI	PPG-Based	6.7	0.6
	4	MDI	PPG-Based	6.5	>5
	5	TDI	PPG-Based	7.47	<0.1
	6	TDI	PPG-Based	7.80	2.2

Example 1

20

[0036] This example shows that structural adhesives exhibiting high ultimate strength on sheet molding compound (SMC) can be prepared with prepolymer compositions according to the invention.

[0037] The following structural adhesive composition was used in the runs:

25

Part A	wt%	Part B	wt%
Prepolymer	60	Arcok® PPG2025	16.7
Aluminum Powder	38	Quadrok®	33.3
Cab-o-sil TS720	2	Microtuff 325F	27
		Cab-o-sil TS720	1
		Aluminum Powder	22

30

[0038] The adhesive was prepared by mixing Part A and Part B in a NCO:OH ratio of 1:0.9 while adding 1 wt% of microbeads (10 mil for CRS substrate, 20 mil for SMC substrate). The adhesive mixture was then applied to one side of a 1"x4" (2.54x10.16 cm) substrate coupon to cover at least 0.5 in² (3.23 cm²) of area then mated with a second substrate coupon to give a total lapshear overlap of 0.5 in² (3.23 cm²). Sample was cured at room temperature and 50% humidity. Samples prepared and tested for lap shear strength according to ASTM D1002 after 1 day and 7 days. All tested done at room temperature (RT).

35

Table 2

Prepolymer	Substrate	Cure	Shear strength (psi) after 1 day	Shear strength (psi) after 7 day
5	SMC	RT	614 (92)	701 (79)
6	SMC	RT	486 (69)	526 (72)
5	SMC	Heat*	656 (92)	643 (32)
6	SMC	Heat*	475 (25)	425 (17)

*Heat cured at 120 °C, 30 min; aged at room temperature

40

[0039] The data in Table 2 shows that Prepolymer 5 according to the invention gave superior shear strength to Prepolymer 6 after room temperature curing and aging for 1 day and 7 days as well as after heat cure (120°C, 30 min) then room temperature aging for 1 day and 7 days.

45

Example 2

50

[0040] This example shows that structural adhesives exhibiting fast room temperature cure on zinc cold rolled steel (Zn CRS) can be prepared with prepolymer compositions according to the invention.

[0041] The structural adhesive formulation and procedure used in this Example was the same as that of Example 1.

Table 3

Prepolymer	Cure	Shear strength (psi) after 1 day	Shear strength (psi) after 7 day	% cure (1d/7d)
1	RT	1324	1617	82
2	RT	874	1684	52
3	RT	1240	1452	85
4	RT	981	1367	72

[0042] The structural adhesives containing Prepolymers 1 and 3 according to the invention showed faster room temperature development of strength after 1 day (% cure (1d/7d)) than those containing prepolymer 2 and 4 compositions.

STATEMENT OF INDUSTRIAL APPLICATION

[0043] The invention provides an improved structural polyurethane adhesive.

Claims

1. In a non-solid structural polyurethane adhesive composition comprising a polyurethane prepolymer reaction product of a polyisocyanate and a polyol composition and a curative for isocyanate groups, the improvement which comprises a polyurethane prepolymer reaction product consisting essentially of at least 80 wt% perfect prepolymers and less than 2 wt% free polyisocyanate monomer.
2. The structural adhesive of Claim 1 in which the polyurethane prepolymer reaction product consists essentially of at least 90 wt% perfect prepolymers.
3. The structural adhesive of Claim 1 in which the polyurethane prepolymer reaction product consists essentially of less than 0.5 wt% free polyisocyanate monomer.
4. The structural adhesive of Claim 1 in which the polyisocyanate is hexamethylene diisocyanate, phenylene diisocyanate, toluene diisocyanate (TDI) 4,4'-diphenyl-methane diisocyanate (MDI), isophorone diisocyanate (IPDI) or bis-(4-isocyanatocyclohexyl) methane.
5. The structural adhesive of Claim 1 in which the polyol is a polyether polyol or a polyester polyol.
6. The structural adhesive of Claim 5 in which the polyol is a polyether polyol or a polyester polyol.
11. A method for adhesively joining or sealing two substrates using a structural polyurethane adhesive composition which comprises applying onto a substrate the non-solid structural polyurethane adhesive composition of Claim 1, and contacting the adhesive composition disposed on the substrate to a second substrate such that a bond is formed.
12. The method of Claim 11 in which the polyurethane prepolymer reaction product consists essentially of at least 90 wt% perfect prepolymers.
13. The method of Claim 11 in which the polyurethane prepolymer reaction product consists essentially of less than 0.5 wt% free polyisocyanate monomer.
14. The method of Claim 11 in which the polyisocyanate is hexamethylene diisocyanate, phenylene diisocyanate, toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI) or bis-(4-isocyanatocyclohexyl) methane.
15. The method of Claim 11 in which the polyol is a polyether polyol or a polyester polyol.

EP 1 253 159 A1

16. The method of Claim 15 in which the polyol is a polyether polyol or a polyester polyol.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 00 8125

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
A	DE 100 30 908 A (HENKEL KGAA) 8 February 2001 (2001-02-08) * page 2, line 29 - page 3, line 60 * * page 10, line 24 - line 40 * * claim 1; example 2 *	1,4-6, 11,14-16	C08G18/10 C09J175/08
A	GB 2 085 902 A (COLAMCO INC) 6 May 1982 (1982-05-06) * page 1, line 59 - page 4, line 11; example 3 *	1,4-6, 11,14-16	
D,A	US 5 202 001 A (STARNER WILLIAM E ET AL) 13 April 1993 (1993-04-13) * column 2, line 33 - column 53; example 7 *	1,5,6	
D,A	US 5 143 996 A (CHUNG DANIEL A ET AL) 1 September 1992 (1992-09-01) * column 2, line 55 - column 3, line 47 * * example 5 *	1,4-6, 11,14-16	

The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	19 July 2002	Neugebauer, U	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
Z : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	S : member of the same patent family, corresponding document		

EPO/EPU 152002 (04/2001)

BEST AVAILABLE COPY

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 00 8125

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
 The members are as contained in the European Patent Office EDP file on
 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-07-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
DE 10030908	A	08-02-2001		DE 10030908 A1 AU 6688000 A BR 0012089 A WO 0102458 A1 EP 1189961 A1 NO 20016418 A TR 200103451 T2	08-02-2001 22-01-2001 02-04-2002 11-01-2001 27-03-2002 28-02-2002 22-04-2002
GB 2085902	A	06-05-1982		AU 548942 B2 AU 7677081 A DE 3141887 A1 ES 498322 D0 ES 8202574 A1 FR 2492834 A1 IT 1141985 B JP 57100120 A US 4395530 A ZA 8107360 A	09-01-1986 29-04-1982 12-08-1982 01-02-1982 01-05-1982 30-04-1982 08-10-1986 22-06-1982 26-07-1983 27-10-1982
US 5202001	A	13-04-1993		US 5051152 A AU 627361 B2 AU 6300890 A BR 9004691 A CA 2025691 A1 DE 69007392 D1 DE 69007392 T2 EP 0420026 A2 ES 2053045 T3 JP 1791999 C JP 3128917 A JP 5001807 B KR 9306919 B1 MX 168620 B ZA 9006854 A	24-09-1991 20-08-1992 11-04-1991 10-09-1991 27-03-1991 21-04-1994 23-06-1994 03-04-1991 16-07-1994 14-10-1993 31-05-1991 11-01-1993 24-07-1993 01-06-1993 29-04-1992
US 5143996	A	01-09-1992		US 4923756 A AT 102963 T DE 3888427 D1 DE 3888427 T2 EP 0304083 A2 ES 2052655 T3 JP 1069342 A JP 1970903 C JP 6088387 B KR 9200621 B1	08-05-1990 15-04-1994 21-04-1994 06-10-1994 22-02-1989 16-07-1994 15-03-1989 27-09-1995 09-11-1994 17-01-1992

EPO/TOIV/PMS

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

BEST AVAILABLE COPY